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Thermochemical Studies on Rare Earth Diglycolate Complexes.

II. Enthalpy and Heat Capacity Changes at 5, 20, 35, and 50 °C.

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The changes in enthalpy and heat capacity for the formation of Pr(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), and Lu(III) diglycolate complexes have been determined at 5.00, 20.00, 35.00, and 50.00 °C. All data refer to an aqueous sodium perchlorate medium with the sodium ion concentration equal to 1.00 M. The enthalpy changes were obtained from a direct calorimetric determination using the calorimeter and titration procedure described in a previous communication. The experimental results have been fitted to equations of the type:

$$\Delta H_j^0 = A + BT + CT^2 + DT^3$$

from which the corresponding heat capacity changes have been obtained.

In the preceding communication we reported on the variations of the various stepwise free energy changes, ΔG_{ij}^0 , with temperature for four lanthanoid diglycolato complexes. From the results obtained it was obvious that no reliable calculations of the corresponding enthalpy changes and still less their variations with temperature could be made from data of this type. This conclusion is quite in line with the observations of several other investigators^{1,2,7}. There are in fact very few investigations published where the accuracy of the equilibrium constants has been high enough to establish the temperature dependence of the enthalpy changes in order to obtain the heat capacity changes. One of these few examples is an investigation by Feates and Ives³ who determined the dissociation constants of cyanoacetic acid (5-45 °C) with an accuracy of about 0.02 % in K_a . In most cases even the enthalpy changes themselves, when determined from the temperature variation of equilibrium constants, became very uncertain. Furthermore, comparisons with results obtained by direct calorimetric methods usually show fairly large systematic differences in the enthalpy values^{1,2,4-8}. The systems where accurate thermal data have been obtained from values of $\Delta G^0(T)$ are all so simple that they can be described by one or two equilibria; in most cases protonation equilibria of weak acids.

The data available in the literature on the temperature dependence of the enthalpy changes on complex formation are rather scarce. The results published indicate that the ΔC_{pj}^0 -values for reactions of this type are fairly large and moreover that these values vary significantly with temperature in the range 0-100 °C. One of the aims of the present investigation has been to obtain further

information of this type. By investigating a series of complex formation reactions we have intended to obtain information about the variations of the capacity changes when the central ion is varied.

The stepwise enthalpy changes, ΔH_j^0 , have been determined by a direct calorimetric method at 5, 20, 35, and 50 °C. Nine rare earth diglycolato systems have been investigated, viz. Pr(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), and Lu(III), for four of which the temperature dependences of the stepwise free energy changes have already been reported (preceding publication). The various heats of reaction were determined by use of the calorimeter and titration procedure described earlier⁹. All measurements refer to an aqueous sodium perchlorate medium with 1.00 M total sodium ion concentration. All concentrations, volumes and additions given in this investigation refer to 25 °C as discussed in the preceding publication.

NOTATION AND CALCULATION

The notation used here is the same as before¹⁰.

The enthalpy changes for the various reactions were determined by graphical and numerical methods. The graphical method, outlined earlier¹⁰, was used to determine the enthalpies of protonation of the diglycolate ion, while the numerical methods were used in all other cases.

Two different numerical methods were used, one developed by Arnek¹¹ and the other by Ekström¹². Both methods give a set of "best" least-squares constants. The differences between the two

methods lie in the type of input data used. References 11 and 12 give details of the computing procedures. The enthalpy changes obtained from the two computing methods were essentially the same.

The stability constants, β_j , needed for the calculations were known at all four temperatures only for the Pr(III), Sm(III), Dy(III), and Yb(III) systems. On the basis of these results the following iterative procedure was used to calculate the stability constants and the enthalpy changes for the five remaining systems, for which β_j -values were known only at 20 °C¹³.

A first guess was made of the stability constants at the various temperatures from the known behaviour of the Pr, Sm, Dy, and Yb systems. The over-all enthalpy changes were then calculated. All stepwise complexes are strong and fairly well separated from one another and an error in the stability constants will thus only have a small influence on the enthalpy changes. Improved stability constants were then calculated from the $\log k(T)$ functions obtained from $\Delta H_j^\circ(T)$ -data and the stability constants at 20 °C. A recalculation of the various enthalpy changes using the new set of stability constants did not lead to any significant changes.

The stability constants at 20 °C used for the calculations have been recalculated from data in Ref. 13. The corrected values are given in Table 10. The reasons for the corrections have been outlined in the preceding publication.

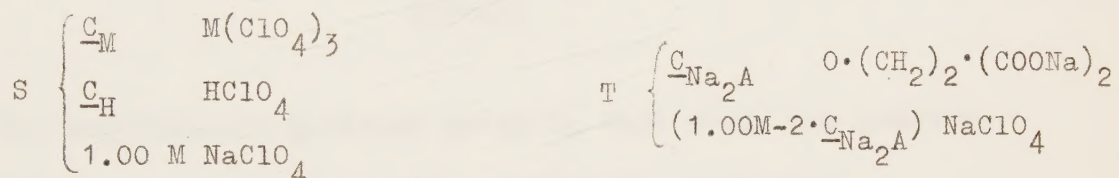
EXPERIMENTAL

Chemicals. Rare earth oxides were obtained from the American Potash & Chemical Corporation. Stock solutions of the rare earth perchlorates were prepared and standardized as described before¹⁴. The diglycolic acid (Fluka AG) was recrystallized from ethyl acetate.

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Stock solutions of the disodium salt of the acid were prepared by neutralization with sodium hydroxide. Sodium perchlorate was prepared as described earlier¹².

Calorimetric titrations. The calorimeter and the experimental procedure used were the same as described before⁹. The measurements have been performed at 5.00, 20.00, 35.00, and 50.00 °C. The calorimeter was filled with 100.24 ml ($\underline{V}_0$) of a solution S. From a calibrated piston burett known volumes ($\underline{v}$) were added of a solution T. For the rare earth diglycolate measurements the solutions S and T had the following composition:



The sodium ion concentration was 1.00 M in all the measurements. The concentrations in the various rare earth perchlorate solutions S are given in Table 5. $\underline{C}_{Na_2A}$ in solution T was 0.3000 M. The compositions of the S and T solutions used for determining the enthalpies of protonation the diglycolate ion are given in Tables 3 and 4.

The solution T was normally added in portions of 1.50 ml at 5 °C and 50 °C and 2.00 ml at 20 °C and 35 °C. Two runs were made for each system at each temperature with about ten additions in each run. The first, third etc. points in Table 6 belong to one titration and the second, fourth etc. points to the second titration. The highest $\bar{n}$ -values reached in the titrations were approximately 2.85.

In order to obtain the heat equivalent of the various systems at least two electrical calibrations were performed in each run. The temperature changes in the calorimeter were small enough to be put proportional to the changes in the resistance of the thermistor.

The heats of dilution of the perchloric acid solutions and the sodium diglycolate solutions were also determined. The results are given in Tables 1 and 2. The heats of dilution of the rare earth perchlorate solutions (S) and the complexes have been neglected¹⁰.

The thermodynamic standard state for the solute species in this study is a hypothetical ideal one molar solution in which the concentration of neutral salt (sodium perchlorate) is equal to 1.0 M.

RESULTS

The experimental Q -values given in this study are positive for exothermal and negative for endothermal reactions.

The proton diglycolate system. The experimental data are given in Tables 3 and 4. The values of Q_{corr} in Table 3 have been obtained from the measured Q -values by correction for the dilution of the perchloric acid solutions. The heats of dilution of the S solutions (Na_2A) are small and can be neglected. In this titration, the highest $\bar{n}_{\text{H}}$ -value reached was 0.6 and, consequently, only ΔH_1^0 could be evaluated.

In the second series, an S-solution of perchloric acid was titrated with a sodium diglycolate solution. The measured Q -values have been corrected for the dilution of the sodium diglycolate solutions and the corrected values are given in Table 4. In this case the heats of dilution of the perchloric acid solutions were neglected. The final $\bar{n}_{\text{H}}$ -values in this titration were all close to 2 and the data were used to determine ΔH_2^0 .

The stepwise enthalpy changes with their estimated errors are given in Table 7. The temperature dependence of the enthalpy changes was described by functions of the type:

$$\frac{\Delta H_j^0}{p_j} = \underline{A} + \underline{B}T + \underline{C}T^2 + \underline{D}T^3 \quad (1)$$

and the various constants are given in Table 8. Expressions for the heat capacity changes, $\frac{\Delta C_{pj}^0}{p_j}$, are obtained by derivation of relation 1 and the values at 25.00 °C are given in Table 9.

The rare earth diglycolate systems. All the experimental $\underline{Q}$ -values corrected for the heats of dilution of the ligand (Table 2) are given in Table 6. Values of the differences ($\underline{Q}_{\text{corr,calc}} - \underline{Q}_{\text{corr,obs}}$) are also given. The stepwise enthalpy changes, $\frac{\Delta H_j^0}{p_j}$, for the various systems with their corresponding standard deviations are shown in Table 7. The standard deviations in the individual measurements, $\underline{\text{Sig}}\underline{Q}_{\text{corr}}$, are included in the last column in this table.

The temperature dependence of the enthalpy changes for the rare earth complexes was described by the same type of relations as for diglycolic acid (eqn. 1) The constants for the various systems are given in Table 8. The heat capacity changes, $\frac{\Delta C_{pj}^0}{p_j}$, at 25.00 °C, obtained from these functions are shown in Table 9.

Precision of the results. The values of $\underline{\text{Sig}} \underline{Q}_{\text{corr}}$ given in Table 7 are useful for an estimate of the precision of the enthalpy titrations. It is obvious that some results are more precise than others.

There are several possible reasons for the deviations, e.g. errors in the concentrations of the reacting species, errors in the stability constants used and temperature errors in the heat exchange device. We do not think that any of these errors alone can be large enough to cause differences in the precision between

the various systems investigated. A combination of error sources seems to be a possible explanation of the observed variations in $\text{Sig } Q_{\text{corr}}$.

The increase of $\text{Sig } Q_{\text{corr}}$ with increasing temperature is another characteristic feature. This is caused by the decrease in the sensitivity of the thermistor with increasing temperature and hence a decreased accuracy. This has been observed earlier⁹. It should be noticed that the errors discussed here are all very small.

In Figure 1, $\frac{\Delta h_v}{v}$ has been plotted as a function of $\bar{n}$ for the praseodymium diglycolate system at four temperatures. The Q -values used for the calculations have been corrected for both the heats of dilution and protonation. The smooth curves have been calculated from the enthalpy changes given in Table 7 and the stability constants given in the preceding publication. The radii of the circles in the figure do not represent error limits; the errors estimated from the experiments are approximately three times smaller.

The enthalpy changes at 25 °C, obtained from the temperature functions in this study, agree fairly well with those determined earlier⁶. The deviations in the over-all ΔH_1^0 and ΔH_2^0 -values between the two studies are all within three standard deviations (3 σ). The deviations in the over-all ΔH_3^0 -values, however, are larger and of the magnitude 0.3 kcal·mol⁻¹. The latter differences are mainly caused by the lack of correction for the heats of protonation in the earlier study.

Determination of the $\Delta H^0(T)$ functions. The temperature dependences of the stepwise enthalpy changes for the systems investigated have all been described by the same type of relations (eqn. 1). The experimental enthalpy data could not be fitted to polynomials of lower than third degree with preservation of the accuracy given by the experiments.

The corresponding heat capacity data are thus described by second degree polynomials. Plots of ΔC_{pj}° vs. T show in most cases minima at around 30 °C. There are a few exceptions, however, where the minima fall outside the temperature range investigated. This is explained by the fact that even very slight errors in the enthalpy changes are enough to cause a substantial shift of the position of the inflection points of the $\Delta H^{\circ}(T)$ -curves. The estimated errors in the ΔC_{pj}° -values are $\pm(1 \text{ to } 2) \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ in the middle of the temperature range investigated and $\pm 4 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at the extreme temperatures.

In the dysprosium system there is some kind of systematic errors in the ΔH_1° -values, which in turn also affect the ΔH_2° -values. The temperature dependences of the enthalpy changes are described by polynomials of the same degree as for the other systems, but the shapes of the curves are different. A straight forward fit of the experimental data to these functions would give maxima instead of minima in the heat capacity changes at around 25 °C for the first two reaction steps. The temperature variations of the heat capacity changes ΔC_{p1}° and ΔC_{p2}° for the dysprosium system are thus quite contrary to the corresponding variations for all of the other systems investigated. In view of the great similarities between the complexes in this study this behaviour is, in our opinion, not very probable. For this reason we have forced the enthalpy changes ΔH_1° and ΔH_2° for the dysprosium system to adopt the same type of temperature dependence as the other systems investigated. The corrections are small and lead to temperature functions (Table 8) which can represent the experimental ΔH_1° -values within $50 \text{ cal}\cdot\text{mol}^{-1}$.

For ytterbium the same type of deviations are present for the first two reaction steps, but only for the values at 20 °C.

DISCUSSION

The earlier observed variation patterns of the quantities $\underline{\Delta G}_j^0$, $\underline{\Delta H}_j^0$, and $\underline{\Delta S}_j^0$ for the formation of diglycolate complexes through the lanthanoid series are on the whole unchanged in the temperature range investigated. It thus seems as if the causes responsible for the observed effects are substantially unaffected by changes of temperature in this range.

The changes in free energy, enthalpy and entropy are not constant with temperature; on the contrary fairly large variations are observed. The temperature dependence of the various stepwise enthalpy changes is best illustrated by the corresponding heat capacity changes at 25 °C shown in Figure 2. The curve representing $\underline{\Delta C}_{p1}^0$ shows the presence of three different regions in the lanthanoid series; two with approximately constant values of $\underline{\Delta C}_{p1}^0$ at the beginning and at the end of the series and one of transition in between. The regions coincide with those observed in the variations of $\underline{\Delta S}_1^0$ through the rare earth series.

The variations of $\underline{\Delta C}_{p2}^0$ and $\underline{\Delta C}_{p3}^0$ through the series are quite different (vide Figure 2). A remarkable feature is the maximum in $\underline{\Delta C}_{p2}^0$ and the minimum in $\underline{\Delta C}_{p3}^0$ which both are formed in the region terbium-ytterbium. It thus seems as the species responsible for this behaviour might be the second complex, acting as a product in the second reaction step and as a reactant in the third.

Another feature is that the heat capacity changes in general decrease in the order $\underline{\Delta C}_{p1}^0 > \underline{\Delta C}_{p2}^0 > \underline{\Delta C}_{p3}^0$. The only exception is found for the formation of the first and second dysprosium and holmium complexes (vide Fig. 2). (The same behaviour is shown by the terbium and erbium complexes at 5 °C.)

The values of ΔC_{pj}^0 are temperature dependent. However, the variation with temperature is fairly small and the above conclusions about the variation within the lanthanoid series are valid in the entire temperature range 5 - 50 °C. The $\Delta C_{pj}^0(T)$ curves have for most of the reactions investigated (including the protonation of diglycolate) a minimum near 30 °C (vide p. 8). Such minima have been observed earlier for other systems in the same temperature range, e.g. by Feates and Ives³. The fact that the minimum occurs at the same temperature in a number of different systems, (with differences in both the ionic strength and the kind of neutral salt used), indicates that this particular behaviour is caused by some property of the solvent.

A quantitative explanation of the observed variations in ΔC_{pj}^0 through the lanthanoid series can not be obtained from the theoretical electrolyte models presently available. We have to know at least which of the species participating in the reactions that is responsible for the variations and this information is at the moment not available. For this reason an investigation of partial molal heat capacities has been started at this laboratory and the results will be published in a future paper.

Various theoretical attempts have been made to describe the thermodynamics of complex formation and protonation reactions. Gurney¹⁵ and Hammett¹⁶ explained, e.g. the minimum in $\log k = f(T)$ for protonation reactions by assuming that the changes in free energy, enthalpy and entropy were sums of terms depending on electrostatic, covalent and cratic effects¹⁵. The only temperature dependent term according to this model is that due to electrostatic effects,

the temperature variation of which is given by the temperature variation of the macroscopic dielectric constant, ϵ , of the medium¹⁶. Around room temperature, the temperature dependence can be expressed by the empirical relation $\epsilon = \epsilon_0 \cdot e^{-T/a}$ for several common solvents (Ref. 15, p. 16 and 28). The model has lately been used by Nancollas¹⁷ and Anderegg¹⁸ for a number of complex formation reactions.

The following relation between the heat capacity change and the entropy change is valid provided that all interactions are electrostatic.

$$\Delta C_p = (\Delta S - \nu \cdot 7.9) \cdot T/e \quad (2)$$

If the interactions are covalent only, the value of ΔC_p is equal to zero. (vide ref. 18 p. 1859 for further details).

The theory can roughly describe the magnitudes of ΔC_{p1}^0 for the reactions in this study, if one assumes that the interactions are mainly electrostatic. The theory can on the other hand neither describe the variations of ΔC_{pj}^0 through the lanthanoid series nor the fact that ΔC_{p3}^0 is negative. Hence it might be concluded that the quantitative success of the model is not too impressive. This might in part be due to the presence of complicating factors such as changes in hydration which are not included in the original model.

In the preceding publication we have already mentioned the difficulties in interpreting macroscopic thermodynamic data in terms of microscopic entities. Such interpretations, necessarily very qualitative, must be made with great care and with full insight into the limitations of the discussions based on the conversion from the macroscopic to the molecular level. It is obviously

very easy to go too far with this type of speculation, particularly because of the ease of producing "theoretical treatment" of the experimental results. The publication of Holzer and Emerson¹⁹ over the use (or mis-use) of the concept of water structure given by Frank and Evans²⁰ is in that part instructive reading.

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Table 1. The heats of dilution of the perchloric acid solutions.

S: 1.00 M NaClO₄
T: C_H = 0.1014 M, C_{Na} = 1.00 M

Temperature →	5 °C	20 °C	35 °C	50 °C
$\frac{V_{tot}}{ml}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$
1.50	0.007			0.004
2.00		0.006	0.005	
3.00	0.007			0.004
4.00		0.005	0.005	
6.00	0.006	0.005	0.004	0.004
9.00	0.006			0.003
12.00	0.006	0.005	0.004	0.003
15.00	0.006			0.003
18.00		0.004	0.004	
20.00		0.004	0.003	

Table 2. The heats of dilution of the sodium diglycolate solutions.

S: 1.00 M NaClO₄
T: C_A = 0.3000 M, C_{Na} = 1.00 M

Temperature →	5 °C	20 °C	35 °C	50 °C
$\frac{V_{tot}}{ml}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$	$\frac{Q}{cal}$
1.50	0.009			-0.018
2.00		-0.008	-0.030	
3.00	0.007			-0.016
4.00		-0.007	-0.028	
6.00	0.005	-0.007	-0.026	-0.014
9.00	0.003			-0.013
12.00	0.002	-0.006	-0.021	-0.012
15.00	0.001			-0.011
18.00		-0.005	-0.017	
20.00		-0.005	-0.016	

Table 3. Corresponding values of $\underline{v}_{\text{tot}}$ and $\underline{Q}_{\text{corr}}$ for the proton diglycolate system at the temperatures 5, 20, 35, and 50 °C.

S: $\underline{C}_{\text{A}} = 0.0300 \text{ M}$; $\underline{C}_{\text{Na}} = 1.00 \text{ M}$

T: $\underline{C}_{\text{H}} = 0.1014 \text{ M}$; $\underline{C}_{\text{Na}} = 1.00 \text{ M}$

Temperature	5 °C	20 °C	35 °C	50 °C
$\frac{\underline{v}_{\text{tot}}}{\text{ml}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$
1.50	-0.014			-0.247
2.00		-0.117	-0.220	
3.00	-0.009			-0.242
4.00		-0.129	-0.216	
4.50	-0.022			-0.245
6.00	-0.020	-0.121	-0.212	-0.234
7.50	-0.014			-0.234
8.00		-0.120	-0.201	
9.00	-0.001			-0.225
10.00		-0.114	-0.206	
10.50	-0.000			-0.212
12.00	0.006	-0.102	-0.191	-0.215
13.50	0.007			-0.202
14.00		-0.094	-0.183	
15.00	0.014			-0.197
16.00		-0.086	-0.162	
18.00		-0.084	-0.158	
20.00		-0.062	-0.146	

Table 4. Corresponding values of $\underline{v}_{\text{tot}}$ and $\underline{Q}_{\text{corr}}$ for the proton diglycolate system at the temperatures 5, 20, 35, and 50 °C.

S: $\underline{C}_{\text{H}} = 0.0916 \text{ M}$, $\underline{C}_{\text{Na}} = 1.00 \text{ M}$

T: $\underline{C}_{\text{A}} = 0.0300 \text{ M}$, $\underline{C}_{\text{Na}} = 1.00 \text{ M}$

Temperature →	5 °C	20 °C	35 °C	50 °C
$\frac{\underline{v}_{\text{tot}}}{\text{ml}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$	$\frac{\underline{Q}_{\text{corr}}}{\text{cal}}$
1.50	0.038			-0.101
2.00		-0.015	-0.069	
3.00	0.036			-0.099
4.00		-0.013	-0.066	
4.50	0.035			-0.098
6.00		-0.012	-0.061	

Table 5. The composition of the various rare earth perchlorate solutions (solutions S) at the temperatures 5, 20, 35, and 50 °C.

Temperature →	5,50 °C		20,35 °C	
Metal Ion	$\frac{C_{Na}}{M} = 1.00 \text{ M}$			
	$\frac{C_M \cdot 10^3}{M}$	$\frac{C_H \cdot 10^3}{M}$	$\frac{C_M \cdot 10^3}{M}$	$\frac{C_H \cdot 10^3}{M}$
Pr	13.59	0.852	18.12	1.136
Sr	14.16	1.080	18.88	1.440
Cd	12.05	0.852	16.07	1.136
Tb	13.94	1.568	18.58	2.090
Dy	14.22	0.426	18.96	0.568
Ho	14.25	1.611	19.00	2.148
Er	12.47	0.681	16.63	0.908
Yb	14.40	0.783	19.20	1.044
Lu	13.07	0.941	17.41	1.254

Table 6. Corresponding values of v_{tot} , Q_{corr} , and $(Q_{calc} - Q_{obs}) = \Delta Q$ for the various rare earth diglycolate systems at 5, 20, 35, and 50 °C.

Temp. °C	Pr		Sm		Eu		Tb		Dy		Ho		Er		Y		Lu	
	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$	$\frac{Q_{corr}}{cal.}$	$\Delta Q \cdot 10^3$
5 °C																		
0.75	283	-1	379	-2	239	-8	14	-6	-124	+21	-164	-18	-189	-18	-174	-3	-154	-5
1.50	526	+6	749	+9	494	-4	62	+6	-171	+19	-306	+7	-347	-14	-352	+11	-206	-6
2.25	569	+7	768	-2	546	+5	180	-1	-49	+11	-172	-1	-256	+2	-317	+8	-238	-6
3.00	581	-5	784	-7	614	+11	286	+10	197	-20	-44	-1	-145	+8	-261	-5	-181	-5
3.75	580	-4	794	+0	711	-3	401	-7	234	-12	81	+2	-28	+15	-203	-9	-123	+3
4.50	580	-4	814	+3	795	+1	541	-7	778	-20	204	+9	108	+11	-136	-9	-48	-1
5.25	581	-6	844	-2	883	-3	647	+6	515	-15	341	+2	250	+8	-57	-12	10	+17
6.00	566	+2	864	+0	960	-12	769	-1	645	-5	478	-4	404	+3	14	+0	80	+17
6.75	545	+9	875	+2	982	+3	879	-6	761	+13	604	+2	587	-16	91	+8	166	+17
7.50	531	-5	875	-6	960	+7	971	-9	884	+13	741	-2	773	-11	178	+14	260	+16
8.25	480	-1	829	+6	870	+9	1012	+6	989	+10	879	-9	989	-1	301	+12	463	-21
9.00	405	+2	773	-2	758	-11	1030	+6	1070	+4	1004	-6	1226	-2	522	-3	801	-28
9.75	317	+2	674	+2	630	-2	996	+4	1120	-7	1109	+2	1396	+7	883	-18	1175	-24
10.50	212	+4	575	-2	540	-6	934	-1	1124	-5	1190	+10	1477	-1	1257	-7	1333	-24
11.25	179	-6	483	+3	434	+4	860	+1	1086	+14	1234	+17	1418	-11	1486	-8	1259	+1
12.00	150	-1	424	-8	310	+9	792	-5	1053	+0	1257	-3	1139	+14	1517	-3	1091	+11
12.75	95	+3	347	+2			692	-10	966	-71	1208	-15			1400	+7	657	+32
13.50	71	+3	275	+4											1177	+9	633	+31
14.25	57	-2	203	-2											881	+18	444	+31
15.00	45	-4	151	+4													333	+1
Temp.																		
20 °C																		
1.00	214	+13	352	-3	164	-9	-141	+6	-297	+4	-374	-8	-405	-9	-376	-6	-329	-10
2.00	459	-4	701	+3	340	+4	-210	+3	-553	+16	-706	+9	-759	-12	-730	-6	-640	-7
3.00	470	-11	715	+2	423	+0	-71	-4	-359	-9	-546	-10	-634	-12	-669	-5	-580	+1
4.00	462	+2	734	+3	527	+1	85	-4	-184	-14	-388	-10	-504	+7	-593	-6	-489	-6
5.00	464	+11	767	+2	659	-1	251	-2	-10	-2	-239	+13	-340	+13	-505	-5	-395	-5
6.00	499	-6	795	+18	797	+9	424	+8	189	+2	-38	-1	-150	+12	-418	+12	-295	+7
7.00	519	-3	882	-15	957	-7	625	-6	403	-2	145	+9	47	+17	-300	+7	-183	+10
8.00	525	+8	940	-23	1077	-11	795	+9	611	+4	351	+4	278	+4	-187	+14	-77	+20
9.00	538	-3	976	-27	1126	+6	974	-3	820	+1	554	+4	523	+0	-60	+9	37	+21
10.00	511	+5	957	-3	1129	+3	1110	+4	1015	+4	779	-12	839	-12	64	+15	181	+6
11.00	471	+3	894	+34	1055	+9	1218	-1	1203	-6	983	-0	1252	-30	258	-10	460	-30
12.00	403	+1	841	+28	964	-7	1272	-1	1348	+4	1226	-10	1653	+7	584	-15	1020	-24
13.00	336	-15	786	-3	861	-10	1275	+1	1479	-6	1446	+4	1961	+13	1165	-10	1590	-25
14.00	254	-10	698	-7	753	-9	1255	-7	1539	+10	1652	+2	2069	-1	1776	-26	1755	-29
15.00	193	-6	616	-4	581	+20	1194	+4	1573	+0	1771	+11	1923	-18	2017	-8	1599	+3
16.00	138	+5	552	-15		1126	-10	1538	-13	1809	-1	1439	+23	1977	-8	1334	+20	
17.00	104	+6	460	-9		951	+13	1344	+8	1701	-9			1742	+7	1023	+35	
18.00	74	+8	316	+26										1375	+28	743	+31	
19.00	43	+17												975	+43	518	+32	
20.00	36	+8														366	+23	
Temp.																		
35 °C																		
1.00	89	-4	407,410	-2,-5	15	-11	-274	+0	-422	+4	-502	-8	-518	-21	-492	-4	-451	-9
2.00	172	+1	226	-10	59	-13	-493	-2	-806	+19	-953	-13	-1008	-21	-977	+8	-878	-11
3.00	183	-4	456	-7	247	+5	-372	-6	-679	+7	-847	-2	-901	-15	-907	-10	-809	-9
4.00	185	+8	465	+27	393	+11	-55	-3	-515	-9	-695	-10	-763	-7	-831	-14	-734	+7
5.00	207	+5	550	+8	577	+2	146	+2	-314	-28	-544	+8	-632	+36	-734	-15	-620	+3
6.00	259	+0	658	-18	746	+6	355	+9	-120	-9	-355	+11	-406	+15	-621	-4	-493	+3
7.00	300	+0	658	-18	746	+6	355	+9	120	-6	-150	+15	-205	+34	-487	+5	-372	+17
8.00	349	-2	716	+6	901	-3	574	+6	350	+13	71	+14	37	+24	-362	+30	-237	+16
9.00	373	+2	792	-12	993	+4	768	+6	586	+14	301	+5	311	-1	-236	+44	-99	+1
10.00	379	+0	806	+3	1039	-2	946	+1	815	+9	531	+4	661	-25	-88	+29	19	+10
11.00	364	+0	793	+17	1023	-1	1087	-5	1036	+0	793	-11	1158	-50	73	+20	279	-22
12.00	329	+2	782	+2	965	-15	1196	-8	1260	-10	1089	-19	1671	-6	473	-74	883	-22
13.00	290	-2	765	-24	921	-17	1270	-7	1465	-10	1408	-17	2062	-5	1096	-47	1520	-23
14.00	241	+3	688	+1	820	-6	1321	-15	1611	+5	1688	+3	2155	-1	1766	-31	1668	-8
15.00	208	-3	624	+14	662	+7	1304	+3	1698	-1	1884	+5	1957	+4	1985	+7	1516	+11
16.00	172	-2	576	+0	423	+44	1249	-2	1676	-8	1944	+2	1475	+43	1892	+17	1284	+8
17.00	125	+11	500	-9			1071	+22	1469	+13	1817	+10			1651	+22	1003	+28
18.00	108	-3	367	+13											1346	+20	773	+13
19.00	86	-8	273	-11											1039	+11	567	+20
20.00	60	-2													762	+12	435	+2
Temp.																		
50 °C																		
0.75	-66	+13	11	+9	-121	-5	-325	+4	-437	-6	-478	-9	-487	-12	-472	-6	-449	-2
1.50	-113	+10	66	-19	-216	-9	-593	-16	-834	-15	-929	-10	-944	-21	-934	-2	-870	-7
2.25	-96	+0	82	-16	-162	+3	-526	-8	-767	+5	-850	-13	-877	-11	-884	-9	-804	-14
3.00	-73	-11	96	-1	-58	-8	-429	-5	-640	-10	-768	-4	-779	-4	-819	-12	-743	+2
3.75	-49	-12	126	+14	29	+30	-308	+5	-520	+11	-638	-2	-661	+13	-737	-13	-645	+3
4.50	-18	-2	194	+11	214	-3	-164	+19	-343	+5	-509	+16	-504	+19	-655	+11	-525	+2
5.25	36	+2	269	+18	374	-9	31	+2	-162	+13	-338	+10	-353	+43	-529	+7	-404	+8
6.00	82	+13	360	+11	509	-11	194	+18	47	+4	-172	+18	-166	+55	-416	+23	-292	+20
6.75	125	+10	444	-6	600	-5	373	+4	231	+13	11	+7	76	-26	-313	+37	-193	+29
7.50	161	-5	476	+6	621	+38	510	+9	427	-1	186	+4	294	-18	-205	+34	-86	+18
8.25	170	-3	507	-3	702	-9	656	-13	609	+0	378	-3	663	-27	-80	+10	97	-45
9.00	174	-4	519	-7	723	-15	773	-12	830	-20	629	-24	1134	-18	136	-36	425	-21
9.75	181	-13	520	-12	724	-26	895	-22	1053	-7	909	-14	1492	-8	603	-66	902	-30
10.50	166	-5	512	-14	671	-17	966	+2	1219	-1	1210	-13	1578	+6	1149			

Table 7. The stepwise values of ΔH_i^0 with their corresponding standard deviations for the various rare earth diglycolates at the temperatures 5, 20, 35, and 50 °C. At each temperature the standard deviations SigQ in the Q_{corr} values are also given.

Temperature →	5 °C					20 °C				
Metal Ion ↓	$\frac{-\Delta H_1^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_2^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_3^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\text{SigQ}\cdot 10^3$ cal		$\frac{-\Delta H_1^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_2^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_3^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\text{SigQ}\cdot 10^3$ cal	
Pr	1.280±0.005	1.362±0.005	0.335±0.006	5		0.757±0.008	1.039±0.006	0.331±0.010	9	
Sm	1.673±0.005	2.163±0.005	1.033±0.004	5		1.160±0.015	1.825±0.012	1.070±0.015	17	
Gd	0.976±0.011	2.706±0.005	1.339±0.009	8		0.476±0.010	2.361±0.007	1.482±0.007	10	
Tb	-0.094±0.009	3.049±0.004	1.982±0.007	6		-0.544±0.009	2.625±0.004	2.251±0.007	9	
Dy	-0.574±0.020	2.833±0.009	2.598±0.014	14		-1.084±0.009	2.397±0.004	2.976±0.005	9	
Ho	-0.953±0.014	2.468±0.005	3.350±0.008	9		-1.382±0.009	1.866±0.004	3.793±0.007	9	
Er	-1.027±0.017	1.658±0.006	4.140±0.013	12		-1.466±0.017	1.120±0.006	4.449±0.013	16	
Yb	-0.816±0.013	0.538±0.007	4.507±0.012	11		-1.311±0.016	0.360±0.008	4.489±0.016	17	
Lu	-0.753±0.027	0.734±0.011	4.091±0.026	20		-1.176±0.022	0.430±0.010	4.102±0.023	22	
Diglycolic Acid	-0.143±0.010	0.988±0.030	-	-		-0.644±0.010	0.420±0.030	-	-	

Temperature →	35 °C					50 °C				
Metal Ion ↓	$\frac{-\Delta H_1^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_2^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_3^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\text{SigQ}\cdot 10^3$ cal		$\frac{-\Delta H_1^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_2^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_3^0}{\text{kcal}\cdot\text{mol}^{-1}}$	$\text{SigQ}\cdot 10^3$ cal	
Pr	0.284±0.004	0.791±0.004	0.452±0.005	5		-0.234±0.011	0.494±0.009	0.545±0.014	10	
Sm	0.658±0.011	1.593±0.010	1.225±0.010	13		0.081±0.016	1.361±0.014	1.370±0.015	14	
Gd	-0.034±0.016	2.127±0.010	1.714±0.013	15		-0.602±0.029	1.759±0.020	1.955±0.025	22	
Tb	-0.984±0.007	2.224±0.004	2.651±0.004	7		-1.479±0.015	1.711±0.010	3.057±0.012	12	
Dy	-1.468±0.012	1.830±0.007	3.450±0.010	13		-2.040±0.021	1.424±0.012	3.893±0.018	17	
Ho	-1.788±0.012	1.340±0.007	4.260±0.010	12		-2.222±0.016	0.864±0.010	4.670±0.016	13	
Er	-1.868±0.028	0.730±0.013	4.815±0.024	27		-2.278±0.033	0.374±0.019	5.111±0.034	25	
Yb	-1.683±0.026	0.136±0.015	4.792±0.029	30		-2.158±0.032	-0.040±0.019	5.048±0.042	28	
Lu	-1.599±0.016	0.230±0.006	4.210±0.017	16		-2.050±0.030	0.101±0.016	4.131±0.040	24	
Diglycolic Acid	-1.089±0.010	-0.027±0.030	-	-		-1.641±0.010	-0.574±0.050	-	-	

Table 8. The stepwise enthalpy changes for the various rare earth diglycolates as functions of temperature:

$$\Delta H_1^0 = \underline{A} + \underline{BT} + \underline{CT}^2 + \underline{DT}^3$$

Constants Metal ↓ Ion		ΔH_1^0					ΔH_2^0				
		$\underline{A}$		$\underline{B}$	$-\underline{C} \cdot 10^3$	$\underline{D} \cdot 10^6$	$\underline{A}$		$\underline{B}$	$-\underline{C} \cdot 10^3$	$\underline{D} \cdot 10^6$
		kcal·mol ⁻¹	kcal·mol ⁻¹ ·K ⁻¹	kcal·mol ⁻¹ ·K ⁻²	kcal·mol ⁻¹ ·K ⁻³	kcal·mol ⁻¹	kcal·mol ⁻¹ ·K ⁻¹	kcal·mol ⁻¹ ·K ⁻²	kcal·mol ⁻¹ ·K ⁻³		
Pr	137.928	1.306856	4.237067	4.691358	174.819	1.694176	5.552124	6.123457			
Sm	119.900	1.142185	3.759520	4.246914	159.179	1.505553	4.839253	5.234568			
Gd	68.001	0.631253	2.062471	2.370370	333.248	3.280608	10.887279	12.098765			
Tb	90.724	0.869571	2.845244	3.209877	182.606	1.774823	5.914311	6.666667			
Dy	63.978	0.604455	1.956622	2.222222	14.249	0.052939	0.056764	0.049383			
Ho	74.458	0.706580	2.266098	2.518519	59.668	0.467373	1.298098	1.283951			
Er	69.661	0.648694	2.036622	2.222222	179.921	1.673979	5.280036	5.629630			
Yb	101.812	0.984906	3.217138	3.604938	88.148	0.836912	2.696880	2.913580			
Lu	41.837	0.384392	1.216071	1.382716	66.168	0.572103	1.664338	1.629630			
Diglycolic Acid	221.569	2.178046	7.203716	8.049383	307.695	3.002863	9.867164	10.913580			

Constants Metal Ion ↓	ΔH_3^0				
	$\underline{-A}$	$\underline{B}$	$\underline{-C \cdot 10^3}$	$\underline{D \cdot 10^6}$	
	kcal·mol ⁻¹	kcal·mol ⁻¹ ·K ⁻¹	kcal·mol ⁻¹ ·K ⁻²	kcal·mol ⁻¹ ·K ⁻³	
Pr	212.924	2.105303	6.922738	7.555556	
Sm	180.570	1.775654	5.821404	6.320988	
Gd	114.090	1.121153	3.672267	3.950617	
Tb	175.850	1.738528	5.720000	6.172840	
Dy	170.584	1.712268	5.729084	6.271605	
Ho	100.000	1.031351	3.571253	4.000000	
Er	166.338	1.667354	5.648418	6.271605	
Yb	519.676	5.090126	16.695982	18.172840	
Lu	373.891	3.736225	12.549991	14.034691	
Diglycolic Acid					

Table 9. The stepwise heat capacity changes ΔC_{Pj}° at 25.00 °C.
The errors in the values given are 1-2 cal·mol⁻¹·K⁻¹.

Metal Ion	$\frac{\Delta C_{P1}^{\circ}}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\Delta C_{P2}^{\circ}}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\Delta C_{P3}^{\circ}}{\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$
Pr	31.4	16.4	-7.8
Sm	33.0	15.9	-10.0
Gd	33.5	15.0	-15.1
Tb	29.0	26.0	-26.1
Dy	30.3	32.3	-31.5
Ho	26.9	35.7	-31.5
Er	26.9	26.8	-24.7
Yb	27.9	11.7	-19.4
Lu	28.0	14.2	-8.2
Diglyc. Acid	29.1	29.5	-

Table 10. Stability constants, β_1 , at 20 °C recalculated from data in Ref. 13.

Metal Ion	Constants →	$\frac{\beta_1 \cdot 10^{-5}}{M^{-1}}$	$\frac{\beta_2 \cdot 10^{-10}}{M^{-2}}$	$\frac{\beta_3 \cdot 10^{-13}}{M^{-3}}$
	Gd	3.09	1.08	1.66
	Tb	2.64	1.20	2.56
	Ho	2.49	1.18	2.91
	Er	2.95	1.44	2.55
	Lu	6.21	5.66	2.64

Figure 1. The total molar enthalpy change, Δh_y , as a function of the average ligand number, $\bar{n}$, for the praseodymium diglycolate system at 5, 20, 35, and 50 °C.

Figure 2. The stepwise heat capacity changes, ΔC_{pi}^0 , at 25 °C for the formation of rare earth diglycolate complexes.

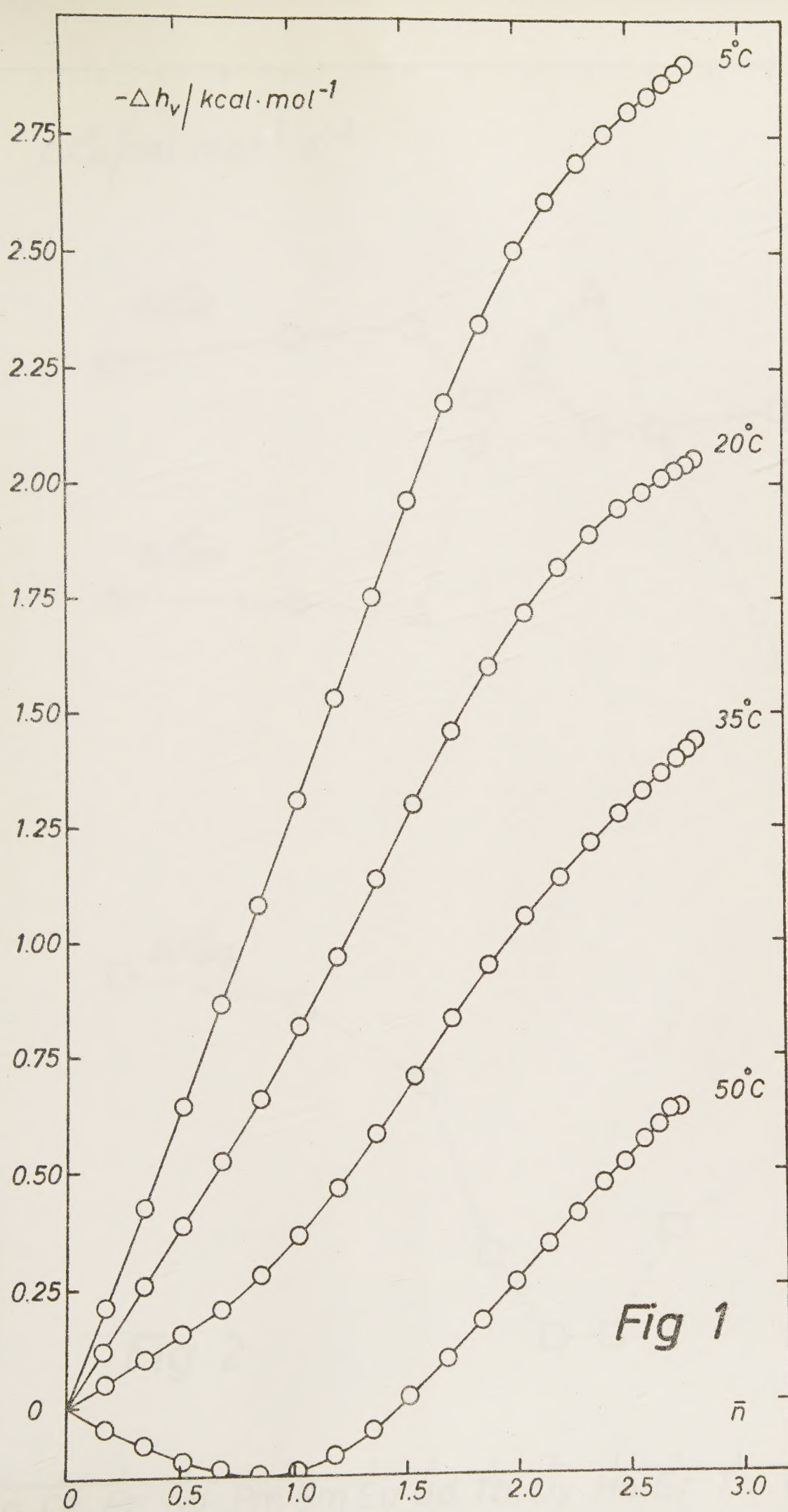


Fig 1

